Interfacial fluctuation effects at 3D wedge-wetting[1]

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Abstract

We review recent advances concerning the nature of fluctuation effects occuring at continuous filling transitions pertinent to fluid adsorption in wedge geometries. Unlike continuous (critical) wetting transitions for planar interfaces which are an extremely rare experimental phenomena, continuous filling transitions should be easily observable in the laboratory since they can occur even if the underlying wetting transition is first order. We argue that interfacial fluctuation effects at filling transitions are extremely strong and lead to a remarkable universal divergence of the interfacial roughness $\xi_\perp \sim (T_F - T)^{-1/4}$ on approaching the transition temperature T_F, valid for all types of intermolecular forces. The results of renormalisation group and transfer matrix calculations of a novel interfacial model yielding a complete classification of the critical exponents for all dimensions and ranges of forces are given.

KEY WORDS: critical exponents; effective interfacial model; filling; interfacial tension; wetting

1 Introduction

After nearly three decades of intense theoretical and experimental scrutiny, it has emerged that there are basically two reasons why it is extremely difficult to observe interfacial fluctuation effects at continuous (critical) wetting transitions in the laboratory [1]. Firstly, critical wetting is a rather rare phenomenon for which no examples are known for solid-liquid interfaces and only a very limited number for fluid-fluid interfaces [2, 3]. Secondly, the influence of interfacial fluctuations in three dimensions ($d=3$) is believed to be rather small [1]. For example, for systems with long-ranged forces, the divergence of the wetting layer thickness ℓ on approaching the wetting temperature T_w is mean-field-like, $\ell \sim (T_w - T)^{-1}$, and the only predicted effect of fluctuations is to induce an extremely weak divergence of the width (roughness) $\xi_\perp$ of the unbinding interface: $\xi_\perp \sim \sqrt{-\ln(T_w - T)}$. Famously, non-classical and strongly non-universal critical exponents are only predicted for systems with strictly short-ranged forces [4], but even here the size of the asymptotic critical regime is very small and beyond the reach of current experimental and simulation methods [3, 5, 6]. Here we review recent theoretical studies [7] of fluctuation effects occuring at continuous (critical) filling or wedge-wetting transitions [8, 9, 10] pertinent to fluid adsorption in wedge geometry and show that the above problems do not arise for filling transitions. First, we emphasise (contrary to previous statements in the literature [9]) that critical filling can occur in systems made from walls that exhibit first-order wetting transitions. This is an extremely important point since it implies that the observation of critical filling transitions is a realistic experimental prospect. Second, we argue that interfacial fluctuations have an extraordinarily strong influence on the character of the filling transition and, in particular in three dimensions, lead to an interfacial roughness $\xi_\perp$ characterising the singularity which diverges with a universal critical exponent. In fact, all the critical exponents are totally different to those believed to occur at critical wetting. The fluctuation theory is based on a) the derivation of a Ginzburg criterion for the self-consistency of mean-field (MF) theory and b) exact transfer matrix analyses and approximate functional renormalisation group calculations of a novel interfacial Hamiltonian model for wedge wetting which has been introduced to account for the highly anisotropic soft-mode fluctuations. This model leads to a complete classification of the critical behaviour in arbitray dimension d and predicts some remarkable fluctuation dominated phenomena which we believe may be tested in the laboratory.

As mentioned above, there are two essential features emerging from the theory of filling whick make the observation of strong interfacial fluctuation effects a realistic experimental possibility. These are:

- The existence of continuous filling transition for wedges made from walls exhibiting first order wetting.
- The enhancement of fluctuation effects at filling as compared to wetting due to the extreme anisotropy of the capillary-wave-like modes.

These points are dealt with separately below.

2 Continuous filling and first-order wetting

To begin, we recall the basic phenomenology of wedge-wetting and highlight the mechanism by which critical filling occurs in wedge geometries even for walls exhibiting first-order wetting transitions. Consider a wedge (in $d=3$ to begin with) formed by the junction of two walls at angles $\pm\alpha$ to the horizontal. Axes (x, y) are oriented across and along the wedge respectively. We suppose the wedge is in contact with a bulk vapour phase at temperature T (less than the bulk critical value T_c) and chemical potential μ. Macroscopic arguments [8, 9] dictate that at bulk coexistence, $\mu=\mu_{sat}(T)$, the wedge is completely filled by liquid for all temperatures $T_c > T \geq T_F$ where T_F is the filling temperature satisfying $\Theta(T_F)=\alpha$. Here, $\Theta(T)$ is the temperature dependent contact angle of a liquid drop on a planar surface. Thus, filling occurs at a temperature lower than the wetting temperature T_w and may be viewed as an interfacial unbinding transition (of first- or second-order) in a system with broken translational invariance. We refer to any continuous filling transition occurring as $T\to T_F$, $\mu\to\mu_{sat}(T_F)$ as critical filling. Also of interest is the complete filling transition which refers to the continuous divergence of the adsorption as $\mu\to\mu_{sat}(T)$ for $T_c>T\geq T_F$ which is known to be characterised by geometry dependent critical exponents [11]. Here, we focus exclusively on critical filling and, in particular, the critical singularities occurring as $t\equiv(T_F-T)/T_F\to 0^+$ at bulk coexistence. The phase transition is associated with the divergence of four lengthscales each characterised by a critical exponent: the mid-point ($x=0$) height of the liquid-vapour interface $\ell_0\sim t^{-\beta_0}$, the mid-point interfacial roughness $\xi_\perp\sim t^{-\nu_\perp}$, the lateral extension of the filled region $\xi_x\sim t^{-\nu_x}$ and the correlation length of the interfacial fluctuations along the wedge $\xi_y\sim t^{-\nu_y}$. So far, there has been no discussion of the values of these critical exponents for three dimensional systems beyond a simple MF calculation for ℓ_0 [9]. On the other hand, transfer-matrix studies [10] in $d=2$ indicate that fluctuation effects are very strong at wedge-wetting and lead to universal critical exponents $\beta_0=\nu_\perp=\nu_x=1$. This is highly suggestive that fluctuation effects play an important role in $d=3$, relevant to experimental studies.

Previous MF analysis [9] have shown that a suitable starting point for the study of wedge-wetting in open wedges (small α) is the interfacial model

$$H[\ell]=\int\!\!\int dx\,dy\;\left[\frac{\Sigma}{2}\,(\nabla\ell)^2+W(\ell-\alpha|x|)\right] \tag{1}$$

where $\ell(x,y)$ denotes the local height of the liquid-vapour interface relative to the horizontal, Σ is the liquid-vapour interfacial tension and $W(\ell)$ is the binding potential modelling the wetting properties of the wall. This model emerges as the appropriate small α limit of a more general drumhead model with perpendicular interaction to the substrate. At MF level, this functional is simply minimised to yield an Euler-Lagrange equation for the y-independent equilibrium height profile $\ell(x)$,

$$\Sigma\,\ddot{\ell} = W'(\ell - \alpha|x|), \tag{2}$$

where the dot and the prime denote differentiation with respect to x and ℓ respectively. This differential equation is solved subject to the boundary conditions $\dot{\ell}(0) = 0$ and $\ell(x) - \alpha|x| \to \ell_\pi$ as $|x| \to \infty$. Here, ℓ_π denotes the MF planar wetting film thickness (*i.e.*, $W'(\ell_\pi) = 0$) and remains microscopic at the filling transition. Integrating once the equation yields a simple equation for the midpoint height,

$$\frac{\Sigma\,\alpha^2}{2} = W(\ell_0) - W(\ell_\pi), \tag{3}$$

which can be solved graphically [9] (see Fig. 1). Note that at bulk coexistence, Young's equation implies $W(\ell_\pi) = -\Sigma\Theta^2/2$ (within the present small angle approximation) so that the present model immediately recovers the macroscopic result $\Theta(T_F) = \alpha$. Depending on the form of $W(\ell)$ (at T_F) the divergence of ℓ_0 as $T \to T_F^-$ is first-order or continuous. The condition for critical filling is that between the global minimum of $W(\ell)$ at ℓ_π and the extremum at $\ell = \infty$ there is no potential barrier. Thus, walls exhibiting critical wetting necessarily form wedges exhibiting critical filling. However, for walls exhibiting first-order wetting, the filling transition is first order or critical depending on whether the transition temperature T_F is greater or lesser than the spinoidal temperature T_s ($< T_w$) at which the potential barrier in $W(\ell)$ appears. Since the macroscopic condition $\Theta(T_F) = \alpha$ implies that T_F can be trivially lowered by making the wedge angle more acute, it follows that walls exhibiting first-order wetting transitions will, in general, exhibit both types of filling transition (see Fig. 2). Note that the tricritical value of the wedge angle α^* separating the loci of first and second-order filling transitions will itself be rather small for weakly first-order wetting so that the Hamiltonian (1) is still valid. The MF value of height critical exponent β_0 for critical filling follows directly from the equation for ℓ_0 if we write the asymptotic decay of the binding potential as $W(\ell) \approx -\, A\,\ell^{-p}$ where A is a (positive) Hamaker constant and p depends on the range of the forces. For systems with short-ranged forces, this decay is exponentially small. A simple calculation then yields $\beta_0 = 1/p$ (quoted in ref. [10] and implicit in reference [9]) so that, for dispersion forces (corresponding to $p = 2$), the MF prediction is $\beta_0 = 1/2$ whilst for short-ranged forces $\beta_0 = 0(\ln)$. The structure of the MF height profile $\ell(x)$ is particularly simple near critical filling [9] and has crucial consequences. In essence, the interface is flat (*i.e.*, $\ell(x) \sim \ell_0$) for $|x| \stackrel{\sim}{<} \ell_0/\alpha$ whilst for $|x| \stackrel{\sim}{>} \ell_0/\alpha$, the height decays exponentially quickly to its asymptotic planar value ℓ_π above the wall. Importantly, the lengthscale controlling this exponential decay is the wetting correlation length $\xi_\| \equiv \sqrt{\Sigma/W''(\ell_\pi)}$ which remains *microscopic* at the filling transition. One consequence of this is that the lateral width of the filled portion of the wedge is trivially identified as $\xi_x \sim 2\ell_0/\alpha$ so that $\nu_x = \beta_0$. More important consequences of the height structure are considered below. In summary, the MF exponents for critical filling so far derived are

$$\beta_0 = \frac{1}{p}, \qquad \nu_x = \frac{1}{p}, \qquad \nu_y = \frac{1}{2} + \frac{1}{p} \qquad\qquad \text{MF.} \tag{4}$$

3 Fluctuation theory for critical filling

We now turn to the main body of our analysis concerning the nature of fluctuation effects at critical filling and consider first fluctuations about the MF profile $\ell(x)$ as measured by the height-height correlation function $H(x, x'; \widetilde{y}) \equiv \langle\, \delta\ell(x,y)\, \delta\ell(x',y')\,\rangle$ where $\delta\ell(x,y) \equiv \ell(x,y) - \langle\, \ell(x,y)\,\rangle$ and $\widetilde{y} \equiv y' - y$. From this, we can extract a Ginzburg criterion for the self-consistency of the theory. To calculate the correlation function, we first exploit the translational invariance along the wedge and introduce the structure factor

$$S(x,x';Q) = \int d\widetilde{y}\; e^{i\,Q\,\widetilde{y}}\, H(x,x';\widetilde{y}). \tag{5}$$

The assumption of MF theory is that fluctuation about $\ell(x)$ are small and hence a Gaussian expansion of $H[\ell]$ about the minimum suffices to determine the correlations. This leads to the differential (Ornstein-Zernike) equation

$$\left(-\Sigma\partial_x^2 + \Sigma Q^2 + W''(\ell(x)-\alpha|x|)\right)\; S(x,x';Q) = \delta(x-x') \tag{6}$$

where we have adsorbed a factor of k_BT into the definitions of Σ and $W(\ell)$. The structure of correlations across the wedge is manifest in the properties of the zeroth moment $S_0(x,x') \equiv S(x,x';0)$ which can be obtained analytically using standard methods. We find

$$S_0(x,x') = \left(|\dot{\ell}(x)| - \alpha\right)\; \left(|\dot{\ell}(x')| - \alpha\right)\; \times \tag{7}$$
$$\left\{ \frac{1}{2\alpha W'(\ell_0)} + \frac{H(xx')}{\Sigma} \int_0^{\min(|x|,|x'|)} \frac{dx}{\left(\dot{\ell}(x) - \alpha\right)^2} \right\}$$

where $H(x)$ denotes the Heaviside step function ($H(x)=1$ for $x \geq 0$, $H(x)=0$ otherwise). From the properties of the equilibrium profile $\ell(x)$, it follows that the lengthscale ξ_x also controls the extent of the correlations across the wedge. In fact, it can be seen that correlations across the wedge are very large and also (essentially) position independent, provided both particles lie within the filled region, implying that, at fixed y, the local height of the filled region fluctuates coherently. On the other hand, the correlations are totally negligible if one (or both) particles lie outside the filled region since their asymptotic decay is controlled by the microscopic length $\xi_\parallel$. These are important remarks central to the development of a general fluctuation theory of wedge-wetting.

Turning next to correlations along the wedge, we note that a simple extension of the above analysis shows that the dominant singular contribution to the structure factor has a simple Lorentzian form

$$S(x,x';Q) \;\approx\; \frac{S_0(0,0)}{1\,+\,Q^2\,\xi_y^2}; \qquad\qquad |x|,|x'| \stackrel{\sim}{<} \xi_x/2, \tag{8}$$

with $S_0(0,0) = \alpha/2W'(\ell_0)$ which shows a very strong divergence as $T \to T_F^-$. The correlation length along the wedge is identified by $\xi_y \approx (\Sigma\ell_0/W'(\ell_0))^{1/2}$. Substituting for the form of $W(\ell)$, and recalling the divergence of ℓ_0 at critical filling, leads to the desired MF result $\nu_y = 1/p + 1/2$ for the correlation length critical exponent as $T \to T_F$ at bulk coexistence. Note that $\xi_y \gg \xi_x$ so that the fluctuations are highly anisotropic and are totally dominated by modes parallel to the wedge direction. The final lengthscale that we calculate within the present MF/Gaussian analysis is the mid-point width $\xi_\perp$ defined by $\xi_\perp^2 \equiv \langle(\ell(0,y)-\ell_0)^2\rangle = H(0,0;0)$ which may be obtained from the Fourier inverse of $S(x,x';Q)$. This leads to the intriguing relation

$$\xi_\perp \;\sim\; \sqrt{\frac{\xi_y}{\Sigma\,\ell_0}} \tag{9}$$

which is one of the central results of this paper. In this way, we are led to the remarkable prediction that the divergence of $\xi_\perp$ at critical filling is universal, independent of the range of the intermolecular forces, and of the form $\xi_\parallel \sim t^{-1/4}$ which should be observable in experimental and computer simulation studies. Thus, to the list (4) we shall add

$$\nu_\perp = \frac{1}{4}, \qquad\qquad \mathrm{MF}. \tag{10}$$

We shall argue below that this result is not affected by fluctuation effects even when MF theory breaks down.

The first step in the development of a fluctuation theory for filling transitions is the derivation of a Ginzburg criterion. The MF analysis presented above should be valid if the fluctuations in the interfacial height are relatively small. Thus, we require $\xi_\perp/\ell_0 \ll 1$ or, equivalently, $t^{1/p-1/4} \ll 1$, implying that MF theory, and the values of critical exponents quoted above are valid in three-dimensions only for $p < 4$. For $p \geq 4$, fluctuation effects dominate and we can anticipate that the roughness $\xi_\perp$ is comparable with the interfacial height ℓ_0. One way of approaching this problem is to formulate a renormalization group theory based on the effective Hamiltonian (1). This is an extremely difficult task and one which we believe is unnecessarily complicated. In view of the extreme anisotropy of fluctuations at filling transitions and their coherent nature across the wedge, we propose that the only fluctuations that are relevant for the asymptotic critical behaviour are those arising from the thermal excitations of the mid-point height $\ell_0(y)$ along the wedge. More specifically, for a constrained non-planar configuration for the mid-point distribution $\{\ell_0(y)\}$, we assume that all other fluctuations are small and, hence, following established methods [12], may be treated in saddle-point approximation. Thus, we are led to a simpler wedge Hamiltonian (of reduced dimensionality), $F[\ell_0(y)] = \min^\dagger H[\ell(x,y)]$ where the dagger denotes the constraint that $\ell(0,y) = \ell_0(y)\ \forall y$. In this way, we have derived the simpler one-dimensional model (of three-dimensional filling)

$$F[\ell_0] = \int dy \left[\frac{\Sigma \ell_0}{\alpha} \left(\frac{d\ell_0}{dy} \right)^2 + V_F(\ell_0) \right] \tag{11}$$

where the coefficient of the gradient term is the local height dependent line tension $\sigma(\ell_0)$ describing the bending energy of long-wavelength fluctuations along the wedge (see below) and V_F is the effective wedge filling potential which has the general expansion

$$V_F(\ell) \;=\; \frac{\Sigma(\Theta^2 - \alpha^2)}{\alpha}\,\ell + \frac{A}{(p-1)\alpha}\,\ell^{1-p} + \cdots . \tag{12}$$

Note that, in the critical regime, $(\Theta(T) - \alpha) \sim t$, so that minimisation of (12) identically recovers the MF result for ℓ_0. For $p = 1$, the second term in (12) is logarithmic whilst for short-ranged forces, it is exponentially small. We comment here that the derivation of the wedge Hamiltonian (11) from the interface model (1) proceeds in a manner directly analogous to the derivation of the interfacial model (1) for wetting from a more microscopic Landau-Ginzburg-Wilson

Hamiltonian which has been discussed in detail by Fisher and Jin [12]. Thus, the full expresion for the line tension term $\sigma(\ell_0)$ in (11) can be written in terms of the planar constrained height profiles $\ell^{(\pi)}(x;\ell_0)$ analogous to the relation of the position-dependent stiffness in the Fisher-Jin theory to the planar constrained magnetisation profile $m^{(\pi)}(z;\ell)$. Thus, we find

$$\sigma(\ell_0) = \Sigma \int_{-\infty}^{\infty} dx \, \left(\frac{\partial \ell^{(\pi)}(x;\ell_0)}{\partial \ell_0} \right)^2 \tag{13}$$

which recovers the position dependence of the first term in (11) for large ℓ_0. The planar constrained profile $\ell^{(\pi)}(x;\ell_0)$ is found from solution to the Euler-Lagrange equation (2) with a constrained boundary condition at $x=0$ such that $\ell^{(\pi)}(0;\ell_0)=\ell_0$.

We propose that the effective Hamiltonian (11) contains all the essential physics associated with the asymptotic critical behaviour at filling transitions. Two checks on this hypothesis are that, in MF and Gaussian approximation, the new model identically recovers the equation for the mid-point height and structure factor emerging from the more complicated model (1) in the same approximation. The great advantage of the new model is, of course, that due to its one-dimensional character, it can be studied exactly using transfer-matrix techniques. The (normalized) eigenfunctions $\psi_n(\ell_0)$ and eigenvalues E_n of the spectrum are found by solving the differential equation (setting $k_B T = 1$ for convenience)

$$-\frac{\alpha\, \psi_n''(\ell_0)}{\Sigma\, \ell_0} + \frac{3\,\alpha\, \psi_n'(\ell_0)}{2\,\Sigma\, \ell_0^2} + V_F(\ell_0)\, \psi_n(\ell_0) \; = \; E_n\, \psi_n(\ell_0) \tag{14}$$

from which the quantities of interest can be calculated. In particular, the probability distribution for the mid-point height $\mathcal{P}(\ell_0) = |\psi_0(\ell_0)|^2$ and the wedge correlation length $\xi_y = 1/(E_1 - E_0)$. The solution of this eigenvalue problem for the wedge potential (12) gives a complete classification of the critical behaviour at critical filling. The calculation confirms that MF theory is valid for $p < 4$, whilst the criticality is fluctuation dominated for $p > 4$ and is characterised by universal critical exponents. The complete list of critical exponents for critical filling in $d=3$ is given by

$$\beta_0 = \tfrac{1}{p}, \quad \nu_x = \tfrac{1}{p}, \quad \nu_y = \tfrac{1}{2} + \tfrac{1}{p} \quad \nu_\perp = \tfrac{1}{4} \qquad\qquad p < 4$$

$$\beta_0 = \tfrac{1}{4}, \quad \nu_x = \tfrac{1}{4}, \qquad \nu_y = \tfrac{3}{4} \qquad \nu_\perp = \tfrac{1}{4} \qquad\qquad p > 4.$$

Note that the universal critical exponents occuring for $p > 4$ are pertinent to critical filling occurring in systems with short-ranged forces and may be tested in Ising model simulation studies similar earlier work on critical wetting [5]. For experimental systems with dispersion forces ($p = 2$), our predictions are $\beta_0 = \nu_x = 1/2$, $\nu_\perp = 1/4$ and $\nu_y = 1$.

To finish our article, we make three final remarks. Firstly, out of bulk two-phase coexistence ($\delta\mu \equiv \mu_{sat}(T) - \mu > 0$) and close to filling, the mid-point height, correlation lengths and roughness show scaling behaviour. For example, in the fluctuation-dominated regime, the solution of (14) shows that $\ell_0 = t^{-1/4}\,\Lambda(\delta\mu\, t^{-5/4})$ where $\Lambda(\zeta)$ is an appropriate scaling function. Thus, along the critical filling isotherm ($T = T_F$, $\delta\mu \to 0$), the height diverges as $\ell_0 \sim \delta\mu^{-1/5}$, which may be easier to observe in experimental and simulation studies. Secondly, the effective filling model that we have introduced can also be used to study complete filling occurring for $T > T_F$ as $\delta\mu \to 0$. The critical behaviour here is found to be MF-like (*i.e.* $\xi_\perp \ll \ell_0$) but also universal, independent of the range of the forces and is consistent with the hypothesis that the geometry of the wedge determines the critical behaviour for this transition [11]. Fluctuation effects at this transition are rather less interesting than for critical filling. Finally, fluctuation model (11) can be generalised to arbitrary bulk dimensions d corresponding to wedges which are translationally invariant in $d-2$ directions. We have studied this model using functional renormalization group techniques and found two fluctuation regimes for general dimension $d < 4$. For $p < p_c \equiv 2(d-1)/(4-d)$, the critical exponent $\beta_0 = 1/p$, corresponding to MF behaviour, whilst for $p > p_c$, the transition is fluctuation dominated and $\beta_0 = (4-d)/2(d-1)$. Importantly, for

$d = 2$, these predictions correspond to the known values of the critical exponents for 2D wedge wetting found from exact transfer-matrix analysis [10] of the full interfacial model (1).

4 Conclusions

We have presented a brief review of the theory for interfacial fluctuation effects at three-dimensional filling and given a complete classification of the possible critical behaviour. We have emphasised two fundamental features of the filling transition which have advantages over the wetting transition as regarding the experimental observation of strong interfacial fluctuation effects. These are the existence of critical filling transitions for wedges made from walls exhibiting first order wetting and the pronounced influence of fluctuation effects due to the extreme anisotropy of interfacial modes which effectively lower the dimensionality of the long-wavelength fluctuations. Consequently, we are confident that the theoretical predictions presented here can be tested experimentally.

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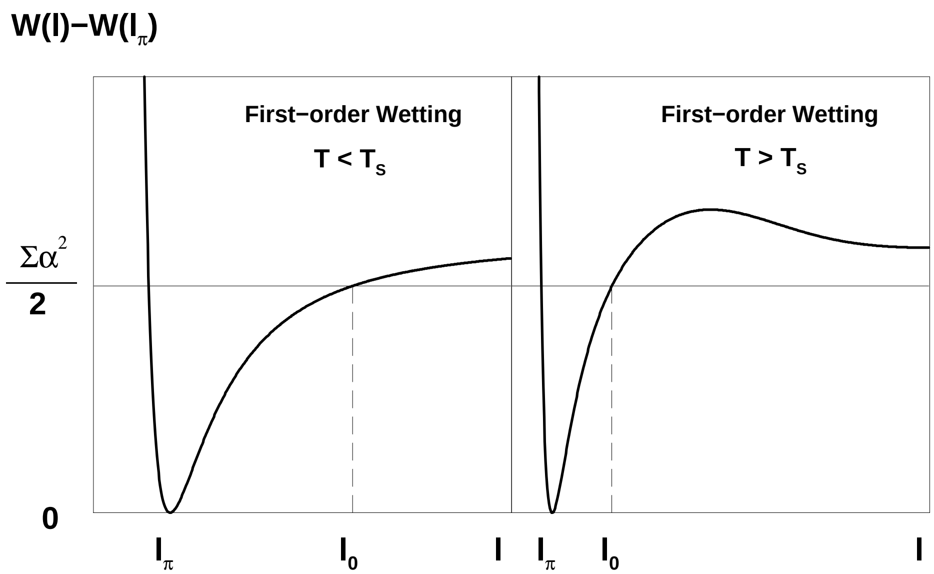

Figure 1: Graphical construction for the mean-field midpoint height ℓ_0 approaching a filling transition for wedges made from walls showing first order wetting. Below the spinoidal temperature T_S, the wetting binding potential has no potential barrier and so the filling transition occuring as $\alpha \to \Theta(T_F)$ is critical.

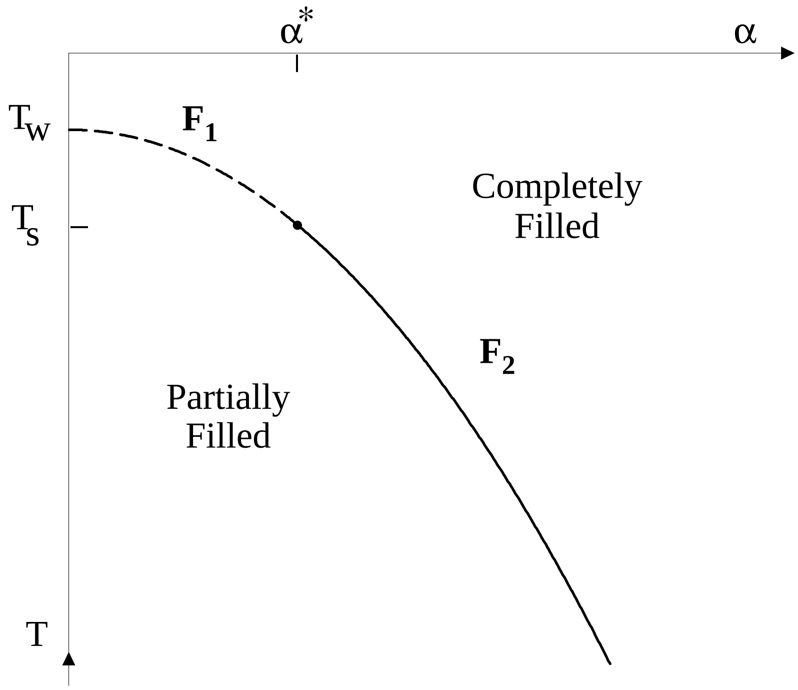

Figure 2: Schematic surface phase diagram showing temperature *vs.* the opening angle α for a system undergoing a first-order wetting transition at T_w in the planar case ($\alpha = 0$). The filling transition is only first-order ($\mathbf{F}_1$) if it takes place at a temperature above the spinoidal temperature T_s but becomes second-order ($\mathbf{F}_2$) if the filling temperature is less than T_s.